論 文 内 容 の 要 旨

ZnO based thin films have attracted many attentions for applications in optoelectronic devices. With wide band gap of ~ 3.37 eV and high exciton binding energy of ~ 60 meV, ZnO is promising material for UV light emission devices and UV laser. Moreover, ZnO can be doped to become sufficiently conductive, with resistivity of ~10^{-4} - 10^{-5} Ωcm, that is especially promising for application as transparent electrodes (TEs). However, electrical and optical properties of ZnO based thin films are very sensitive to crystalline perfections and defects states, which depend on preparation procedures. Though enormous studies have been done on ZnO thin films and gained noticeable progress, the issues on defects, grain boundaries, film crystallinity and their correlations with optoelectrical properties of ZnO based thin films are being challenges and have not been fully elucidated. Better understanding about conducting mechanisms and defects formation are crucial for improving performance of devices based on ZnO films.

One important application of ZnO based thin films is TEs. For this application, ZnO based thin films should have good thermal stability to keep its high transparency and high electrical conductivity under thermal stress during device fabrication. Unfortunately, almost ZnO based thin films showed degradation in electrical properties under annealing. To improve thermal stability of ZnO based TEs, several capping layers including SiO_2, Al_2O_3, zinc tin oxide (ZTO), antimony doped tin oxide (ATO), NiO_x, and TiO_x, or stacking metal layers inside ZnO film such as Au and Cu, have been employed. However, the improvements were not enough, the degradation was still observed, even with thick capping layer (several tens or hundreds nm). Moreover, the degradation mechanism is under debate.

Therefore, this research was carried out in order to

- Improve optoelectrical properties of ZnO based thin films.
- Elucidate the conducting mechanism, the relationship between defects states with optical and electrical properties.
- Get understanding on the thermal degradation mechanism of electrical properties of Al-doped ZnO thin films, which is most promising ZnO based materials for applications as transparent electrodes.
- Improve thermal stability of Al-doped ZnO thin films.

In the first part of this research, we employed Ar plasma treatment in a low vacuum chamber in order to improve optoelectrical properties of ZnO thin films. Evolution of electrical properties of ZnO thin film with plasma treatment time was studied simultaneously with the evolution of photoluminescence properties and surface morphologies, to get insight into the mechanism of the improvement of electrical properties. The variations of optical absorption coefficient and structural properties were also studied. The results show that the Ar plasma treatment in the low vacuum chamber simultaneously enhanced both the electrical properties and the photoluminescence properties of ZnO thin films. Although the Hall mobility and the carrier concentration were increased by the plasma treatment, the evolution of Hall mobility was different from the evolution of carrier concentration. The Hall mobility quickly increased to a saturated value after a short plasma duration, while the carrier concentration continuously increased with further plasma treatment. Identically, the intensity of deep level emissions (DLEs) in photoluminescence of ZnO films quickly decreased and got stable, while the intensity of near band edge emissions (NBEs) continuously increased as the increase in carrier concentration. The steep decrease in DLEs and the quick enhancement in Hall mobility might suggest a quick passivation of deep level defects. Once deep level defects were passivated, optical transitions via deep level defects were suppressed, leading to reduction of DLEs and enhancement in NBEs. Simultaneously, trapped electrons were released, giving rise in Hall mobility and carrier concentration. In addition to the passivation of radiative deep level defects, new

shallow donors were continuously formed, giving continuous rises in the NBEs and carrier concentration, but not contributing to increase in Hall mobility and reduction of DLEs. The increase in NBEs was sufficiently larger than the decrease in DLEs, therefore, beside the passivation of radiative deep level defects, non-radiative defects might be passivated. For further plasma treatment time or high plasma power, the Hall mobility decreased when etching was observed on the surface.

The plasma treatment resulted in the change in absorption coefficient and crystal structure. The excitonic peak in the absorption spectrum was suppressed after plasma treatment, and the absorption edge was shifted to longer wavelength. These results stem from the increase in carrier concentration in the films, owning to screening effect on the Coulombic interactions of excitons. The change in optical absorption coefficient reveal the bulk effect of plasma treatment. Our study also observed the change in lattice constants by plasma treatment, which is another evidence of bulk effect. The *c* lattice constant was increased while *a* lattice constant was decreased. These changes imply that the crystal lattices might bear a compressive stress and were distorted by the plasma treatment. Such the changes could be due to the incorporation of ions/atoms from plasma environment. The data obtained using secondary ion mass spectroscopy confirmed the incorporation of H into ZnO film after the plasma treatment. The penetration depth of H was ~ 100 nm after 5 min plasma treatment, strongly supported for the deep effect of plasma. It was found that He plasma treatment in the low vacuum chamber also enhanced optoelectrical properties of ZnO films. However, O_2 plasma treatment in the low vacuum chamber could not result in such improvement. No enhancement was obtained by Ar plasma treatment in high vacuum chamber. These results, accompanied with higher concentration of H in ZnO film after the Ar plasma treatment in the low vacuum chamber, strongly suggest the effects obtained by the Ar plasma treatment was originated from the defect passivation and donor states of H. This part of the research is presented in chapter 3 of the thesis.

The second part of the research concerns the electrical properties and thermal stability of AZO films. Chapter 4 of the thesis is the study on thermal stability of Al-doped ZnO (AZO) thin films under annealing in N_2 gas, with temperature 300 – 600 °C. To evaluate the effect of crystallinity on the thermal stability, AZO (0.5 wt%) films were deposited using radio frequency superimposed direct current magnetron sputtering at different substrate temperatures (T_S) (200 -300 °C) to obtain different crystallinity. Our results show that the AZO films deposited at higher T_S (250 and 300 °C), which had better *c*-axis orientation, exhibited better thermal stability than the AZO film deposited at lower T_S (200 °C), which had larger titling of grains along c-axis orientation. Both Hall mobility and carrier concentration were decreased with annealing temperature higher than 300 °C for 1 h. The degradation of electrical properties could be attributed to Zn desorption and segregation of atoms at the defects site along the grain boundaries. Using Drude model for optical properties of AZO films, we deduced the optical mobility of charge carrier, which can be considered as in-grain mobility. The optical mobility (μ_{opt}) increased with annealing temperatures, and correspondingly, the mobility through grain boundaries (μ_{GB}) decreased by the annealing, thereby reducing Hall mobility. Sample with higher *c*-axis orientation exhibited higher Hall mobility and could maintained high Hall mobility even after the annealing due to small contribution of grain boundaries. However, in sample with poor orientation, due to large grain boundaries, the μ_{GB} was low, and therefore, Hall mobility was low and became lower after the annealing.

Ultrathin Al films with thickness of 2.2 nm were deposited on the AZO films by magnetron sputtering at room temperature in order to improve thermal stability of AZO films. The ultrathin Al films were dominated by AlO_x state after exposing to the air. The oxidation of Al film was confirmed by X-ray photoelectron spectroscopy (XPS). The ultrathin Al capping layer greatly enhanced the thermal stability of electrical properties of AZO films, while obtaining high transparency comparable with as-deposited AZO films without the Al coating. For all the Al coated AZO samples (Al/AZO), carrier concentration was stable, which was consistent with the transmission spectra of samples in near infrared range. The Hall mobility of Al/AZO films with poor *c*-axis orientation still decreased but remained higher than that of bare AZO films. Improvements in Hall mobility were observed in Al/AZO films with better *c*-axis orientation. A Hall mobility as high as 49 cm^2/Vs was obtained in the Al/AZO sample with AZO layer deposited at T_S of 300 °C only

by annealing at 400 °C in N_2 gas for 1 h. Using thermal desorption spectroscopy (TDS), we found that the Zn desorption from Al/AZO samples was suppressed, due to passivation of ultrathin Al film on surface defects. The passivation of Zn desorption agreed well with the stability of carrier concentration in all Al/AZO samples, suggesting that the reduction in carrier concentration by the annealing at high temperature strongly related to the Zn desorption. The different evolutions of Hall mobility depending on the degree of *c*-axis orientation imply difference in effects of the Al capping layer on grain boundaries. For good *c*-axis oriented films, the Al capping layer effectively passivated the grain boundaries, thereby preventing the segregation at grain boundaries, leading to the increase in Hall mobility. For bad *c*-axis oriented film, the Al capping layer only partially passivated the grain boundaries, therefore, the reduction in Hall mobility was still observed.

Thermal stability of AZO films (T_S = 300 °C) under annealing in air was presented in chapter 5 of the thesis. Compared to the annealing in N_2, annealing in air resulted in stronger reduction in carrier concentration and Hall mobility. The stronger degradation could be attributed to the incorporation of oxygen into AZO layer. The ultrathin Al capping layer exhibited insufficient effects. Though the degradation in ultrathin Al capped AZO sample was much lower than degradation in bare AZO layer, it was still observed with annealing at a high temperature of 500 °C. To further prevent the degradation of electrical properties of AZO layer, thicker Al films with thickness up to 10.8 nm were employed as capping layer, and the passivation effect was studied at annealing temperature of 500 °C for different annealing time. The results show that there were two stages of evolution of electrical properties of Al/AZO films with thick Al capping layer. Firstly, electrical properties of Al/AZO samples were quickly improved and maintain until the sample getting high transparency as that of bare AZO sample. Afterward, the electrical properties started decreasing gradually. The retention of high conductivity in the first stage was attributed to the effect of an oxygen-deficient interface layer, which was formed by interaction and interdiffusion between Al capping layer and bottom AZO layer. This oxygen-deficient layer caused the low transparency of the Al/AZO film because of high absorption in visible range. The oxygen deficient layer captured oxygen atoms migrating from environment, thereby preventing them from migrating into bottom AZO layer. As a result, electrical properties could be improved like in the case of annealing in N_2. Once the oxygen deficient layer was fully oxidized and disappeared, the Al/AZO samples were transparent, and oxygen atoms were no longer captured. The oxygen migrated into bottom AZO layer and caused the degradation. To increase the retention time of the oxygen-deficient interface layer, the Ar plasma treatment in low vacuum chamber was employed. The effect can be attributed to the prevention of the inter-diffusion of atoms between top and bottom layers, owning to the incorporation of H along the grain boundaries which can passivate and block the interaction and diffusion sites. The results of this part of the research imply that employing thin Al film can enhance both electrical properties and their thermal stability of AZO films under annealing, even in air. The grain boundaries and surface defects passivation by the capping layer can help to prevent the degradation caused by thermal excitation, while the oxygen-deficient interface layer help to prevent oxygen migration. These findings can be applied into optoelectronic devices which require high temperature processes.